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**Legacy and emerging perfluoroalkyl substances are
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Legacy and emerging perfluoroalkyl substances are important
drinking water contaminants in the Cape Fear River Watershed of
North Carolina

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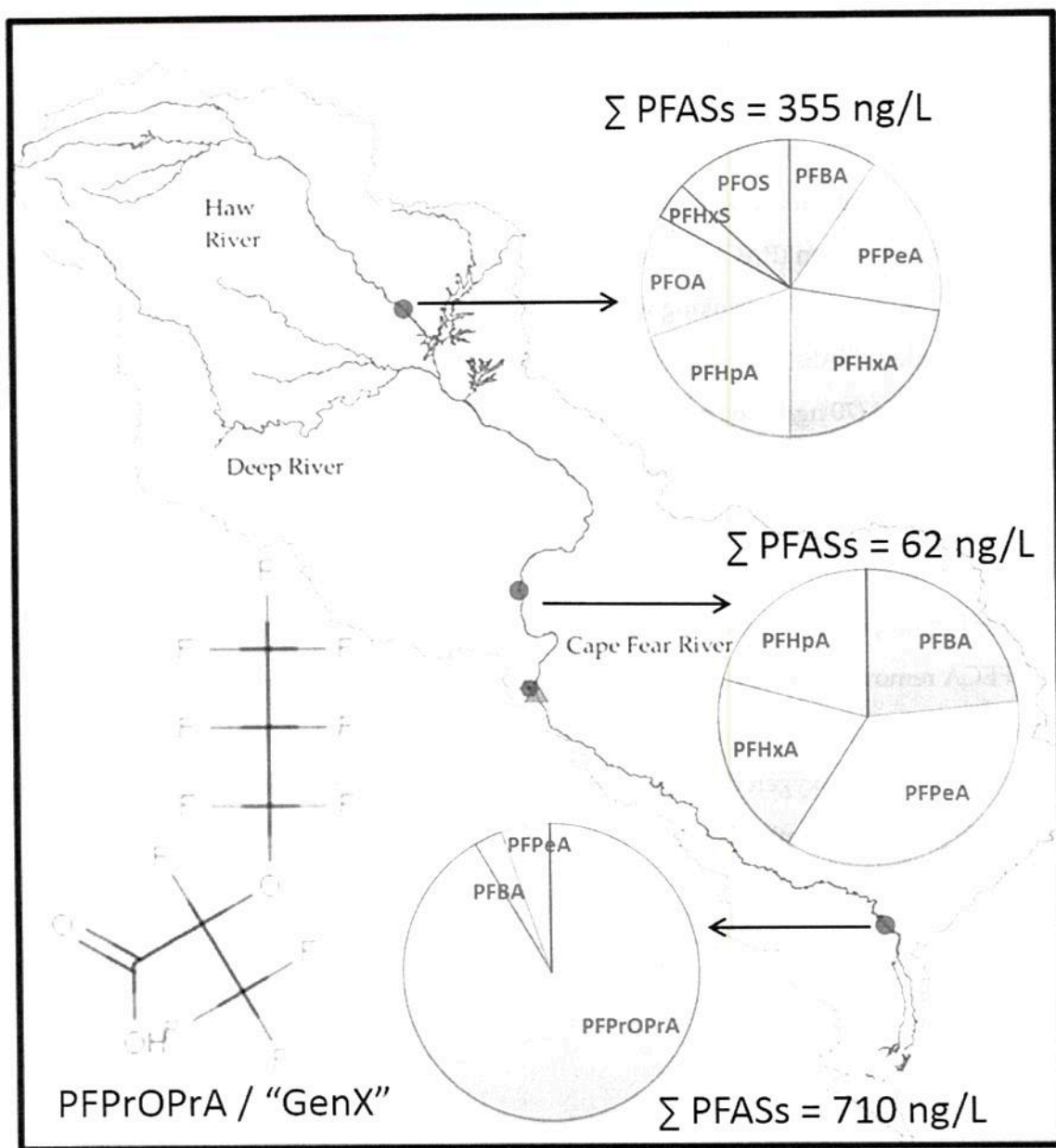
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Abstract

Long-chain perfluoroalkyl substances (PFASs) are being replaced by short-chain PFASs and fluorinated alternatives. For ten traditionally studied PFASs and seven recently discovered perfluoroalkyl ether carboxylic acids (PFECAs), we report (1) occurrence in the Cape Fear River (CFR) watershed, (2) fate in drinking water treatment processes, and (3) adsorbability on powdered activated carbon (PAC). In the headwater region of the CFR basin, PFECAs were not detected in the raw water of a drinking water treatment plant (DWTP), but concentrations of traditionally studied PFASs were high. The US Environmental Protection Agency's lifetime health advisory level (70 ng/L) for perfluorooctane sulfonic acid and perfluorooctanoic acid (PFOA) was exceeded on 57 of 127 sampling days. In raw water of a DWTP downstream of a PFAS manufacturer, the mean concentration of perfluoro-2-propoxypropanoic acid (PFPrOPrA), a replacement for PFOA, was 631 ng/L (n=37). Six other PFECAs were detected with three exhibiting chromatographic peak areas up to 15 times that of PFPrOPrA. At this DWTP, PFECA removal by coagulation, ozonation, biofiltration, and disinfection was negligible. PFAS adsorbability on PAC increased with increasing chain length. Replacing one CF₂ group with an ether oxygen decreased PFAS affinity for PAC, while replacement of additional CF₂ groups with ether oxygens did not lead to further affinity changes.

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Introduction

Perfluoroalkyl substances (PFASs) are extensively used in the production of plastics, water/stain repellents, firefighting foams and food-contact paper coatings. The widespread occurrence of PFASs in drinking water sources is closely related to the presence of industrial sites, military fire training areas, civilian airports, and wastewater treatment plants.¹ Until 2000, long-chain PFASs, such as perfluorocarboxylic acids (PFCAs) with 7 or more carbon atoms and perfluorosulfonic acids (PFSAs) with 6 or more carbon atoms, were predominantly used.² Accumulating evidence about ecotoxicological and human health effects^{3,4} associated with exposure to long-chain PFASs has led to increased regulatory attention. Recently the U.S. Environmental Protection Agency (USEPA) established a lifetime health advisory level (HAL) of 70 ng/L for the sum of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) concentrations in drinking water.^{5,6} Over the last decade, production of long-chain PFASs has declined in Europe and North America, and manufactures are moving towards short-chain PFASs and fluorinated alternatives.⁷⁻¹⁰ Some fluorinated alternatives were recently identified,^{8,11} but the majority of the organofluorine loading to the aquatic environment remains unidentified.¹²⁻¹⁴

One group of fluorinated alternatives, perfluoroalkyl ether carboxylic acids (PFECAs), was recently discovered in the Cape Fear River (CFR) downstream of a PFAS manufacturing facility.¹¹ Identified PFECAs included perfluoro-2-methoxyacetic acid (PFMOAA), perfluoro-3-methoxypropanoic acid (PFMOPrA), perfluoro-4-methoxybutanoic acid (PFMOBA), perfluoro-2-propoxypropanoic acid (PFPrOPrA), perfluoro(3,5-dioxahexanoic) acid (PFO2HxA), perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA) and perfluoro(3,5,7,9-tetraoxadecanoic) acid (PFO4DA) (Table S1 and Figure S1 in supporting information (SI)). The ammonium salt of PFPrOPrA is a known PFOA alternative that has been produced since 2010 with the trade name "GenX".¹⁵ According to the manufacturer, the ether oxygen enables "very rapid bioelimination"¹⁵; however, except for the PFPrOPrA data reported by the manufacturer,¹⁶⁻¹⁸ little information is available on pharmacokinetic behavior, toxicity, or environmental fate and

transport of PFECAs. To the knowledge of the authors, the only other published PFECA occurrence data are for PFPrOPrA in Europe and China,¹⁹ and no published data are available on the fate of PFECAs during water treatment.

The strong C-F bond makes PFASs refractory to abiotic and biotic degradation,²⁰ and most water treatment processes are ineffective for legacy PFAS removal.²¹⁻²⁶ Processes capable of removing PFCAs and PFSAAs include nanofiltration,²⁷ reverse osmosis²⁴, ion exchange,^{27, 28} and activated carbon adsorption,^{27, 28} with activated carbon adsorption being the most widely employed treatment option.

The objectives of this research were to (1) identify and quantify the presence of legacy PFASs and emerging PFECAs in drinking water sources, (2) assess PFAS removal by conventional and advanced processes in a full-scale drinking water treatment plant (DWTP), and (3) evaluate PFAS adsorbability by powdered activated carbon (PAC).

Materials and Methods

Water samples: Source water of three DWTPs treating surface water in the CFR watershed was sampled between June 14 and December 2, 2013 (Figure S2 in SI). Samples were collected from the raw water tap at each DWTP daily as either 8-hour composite (DWTP A, 127 samples) or 24-hour composite (DWTP B, 73 samples; DWTP C, 34 samples). Samples were collected in 250-mL HDPE bottles and picked up (DWTPs A and B) or shipped overnight (DWTP C) on a weekly basis. All samples were stored at room temperature until analysis (within 1 week of receiving). On August 18, 2014, grab samples were collected at DWTP C after each unit process in the treatment train (raw water ozonation, coagulation/flocculation/sedimentation, settled water ozonation, biological activated carbon (BAC) filtration, disinfection by medium pressure UV lamps and free chlorine). Operational conditions of DWTP C on the sampling day are listed in Table S2 in SI. Samples were collected in 1-L HDPE bottles and stored at room temperature until analysis. On the same day, grab samples of CFR water were collected in six 20-L HDPE

carboys at William O. Huske Lock and Dam downstream of a PFAS manufacturing site and stored at 4°C until use in PAC adsorption experiments.

Adsorption experiments: PFAS adsorption by PAC was studied in batch reactors (amber glass bottles, 0.45 L CFR water). PFECA adsorption was studied at ambient concentrations (~1,000 ng/L PFPrOPrA, chromatographic peak areas of other PFECAs ~10-800% of the PFPrOPrA area). Legacy PFASs were present at low concentrations (<40 ng/L) and spiked into CFR water at ~1000 ng/L each. Background water matrix characteristics are summarized in Table S3 in SI. A thermally-activated, wood-based PAC (PicaHydro MP23, PICA USA, Columbus OH, mean diameter: 12 µm, BET surface area: 1460 m²/g)²⁹ proved effective for PFAS removal in a prior study²⁸ was used at doses of 30, 60 and 100 mg/L. These doses represent the upper feasible end for drinking water treatment. Samples were taken prior to and periodically after PAC addition for PFAS analysis.

PFAS analysis: Information about analytical standards and the liquid chromatography-tandem mass spectrometry (LC-MS/MS) method for PFAS quantification is provided in SI.

Results and Discussion

PFAS occurrence in drinking water sources: Mean PFAS concentrations in source water of three DWTPs treating surface water from the CFR watershed are shown in Figure 1. In communities A and B, only legacy PFASs were detected (mean ΣPFAS: 355 ng/L in community A, 62 ng/L in community B). Detailed concentration data are shown in Table S6 and Figure S3 in SI. In community A, PFCAs with 4-8 carbons, perfluorohexane sulfonic acid (PFHxS) and PFOS were detected at median concentrations > QLs. Mean and median concentrations were 44 and 29 ng/L, respectively, for PFOS, and 46 and 34 ng/L, respectively, for PFOA. During the 127-day sampling campaign, the sum concentration of PFOA and PFOS exceeded the USEPA HAL of 70 ng/L on 57 days, and the mean over the entire study period was 90 ng/L. Similar legacy PFAS concentrations were observed in the same area ten years ago,³⁰ suggesting that PFAS source(s) upstream of community A have long-term negative impacts on drinking water quality. Also,

our data show that legacy PFASs remain surface water contaminants of concern even though their production has been phased out in the US. Relating total PFAS concentration to average daily stream flow (Figure S4 in SI) illustrated a general trend of low PFAS concentrations at high flow and high concentrations at low flow, consistent with the hypothesis of upstream point source(s). In community B, perfluorobutanoic acid (PFBA) and perfluoropentanoic acid (PFPeA) were the most frequently detected, with mean concentrations of 12 and 19 ng/L, respectively. Mean and median PFOA and PFOS concentrations were <QL, and the maximum sum concentration of PFOA and PFOS was 59 ng/L. Lower PFAS concentrations in community B relative to community A can be explained by the absence of substantive PFAS sources between the two communities, dilution by tributaries, and the buffering effect of Jordan Lake, a large reservoir located between communities A and B.

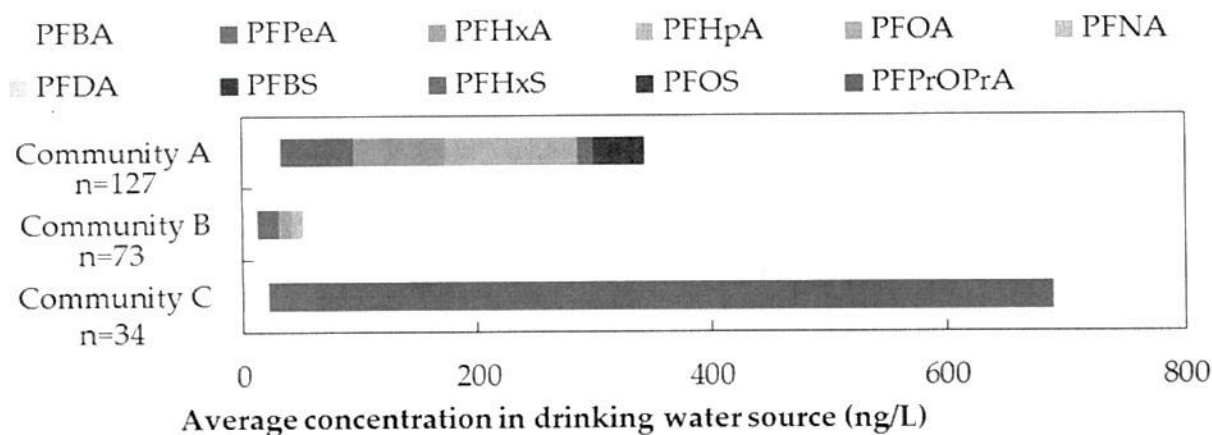


Figure 1. PFAS occurrence at drinking water intakes in the CFR watershed. Concentrations represent averages of samples collected between June and December 2013. Individual samples with concentrations < QLs were considered as 0 when calculating averages, and average concentrations < QLs were not plotted.

In community C (downstream of a PFAS manufacturing site), legacy PFAS concentrations were low, and only mean (and median) concentrations of PFBA and PFPeA were >QLs. However, high concentrations of PFPrOPrA were detected (up to ~4500 ng/L). The average PFPrOPrA concentration (631 ng/L) was approximately eight times the average summed PFCA and PFSA concentrations (79 ng/L). Other PFECAs had not yet been identified at the time of analysis. Similar to communities A and B, the highest PFAS concentrations for community C were also observed at low flow (Figure S3 in SI).

PFAS fate in conventional and advanced water treatment processes: To investigate whether PFASs can be removed from impacted source water, samples from DWTP C were collected at the intake and after each treatment step. Results in Figure 2 suggest conventional and advanced treatment processes (coagulation/flocculation/sedimentation, raw and settled water ozonation, BAC filtration, disinfection by medium pressure UV lamps and free chlorine) did not remove legacy PFASs, consistent with previous studies.²¹⁻²⁵ The data further illustrate that no measurable PFECA removal occurred in this DWTP. Concentrations of some PFCAs, PFSA, PFMOPrA, PFPrOPrA and PFMOAA may have increased after ozonation, possibly due to the oxidation of precursor compounds.²⁴ Disinfection with medium pressure UV lamps and free chlorine (located between BAC effluent and the finished water) may have decreased concentrations of PFMOAA, PFMOPrA, PFMOBA and PFPrOPrA, but only to a limited extent. Results in Figure 2 further illustrate that the PFAS signature of the August 2014 samples was similar to the mean PFAS signature observed during the 2013 sampling campaigns shown in Figure 1; i.e., PFPrOPrA concentrations (400-500 µg/L) greatly exceeded legacy PFAS concentrations. Moreover, three PFECAs (PFMOAA, PFO2HxA and PFO3OA)¹¹ had peak areas 2-113 times greater than that of PFPrOPrA (Figure 2b). The existence of high levels of emerging PFASs suggests the necessity of incorporating them into routine monitoring.

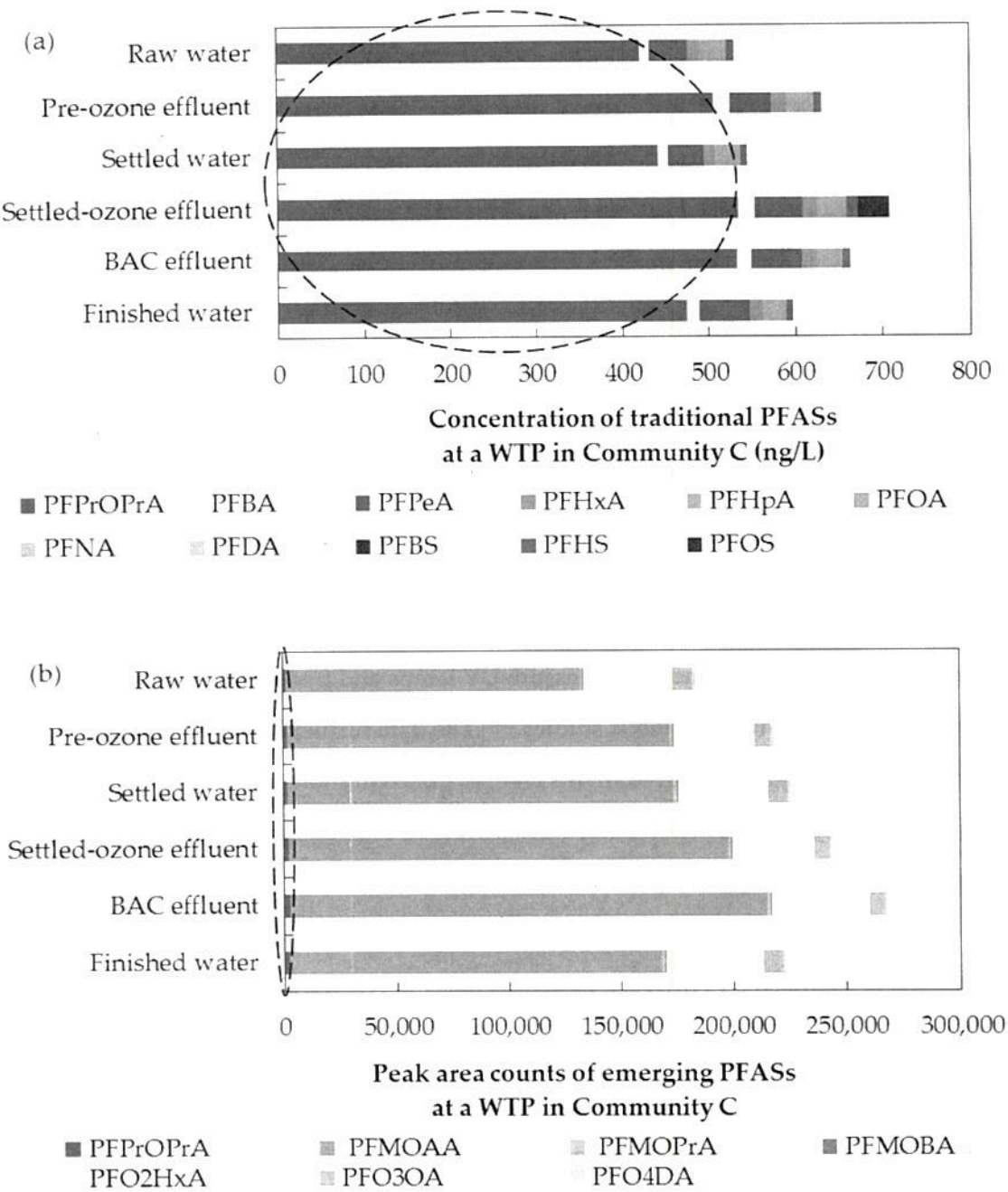


Figure 2. Fate of (a) legacy PFASs and PFPrOPrA and (b) PFECAs through a full-scale water treatment plant. Because authentic standards were not available for emerging PFECAs, chromatographic peak area counts are shown in panel b. PFPrOPrA data are shown in both panels and highlighted in dashed ovals for reference. Compounds with concentrations <QL were not plotted.

177

178 **PFAS adsorption by PAC:** PAC can effectively remove long-chain PFCAs and PFSA, but its
179 effectiveness decreases with decreasing PFAS chain length.^{23, 24, 28} It is unclear, however, how the
180 presence of ether group(s) in PFECAs impacts adsorbability. After a contact time of 1 hour, a
181 PAC dose of 100 mg/L achieved >80% removal of legacy PFCAs with carbon chain length ≥ 7 . At
182 a PAC dose of 60 mg/L, >80% removal was achieved for PFCAs with carbon chain length ≥ 8
183 over the same time. At a PAC dose of 100 mg/L, removals were 95% for PFO₄DA and 54% for
184 PFO₃OA, but <40% for other PFECAs. Detailed removal percentage data as a function of PAC
185 contact time are shown in Figure S5 in SI. PFMOAA could not be quantified by the analytical
186 method used in this test; however, based on the observations that PFAS adsorption decreases
187 with decreasing carbon chain length and that PFECAs with one or two more carbon atoms than
188 PFMOAA (i.e., PFMOPrA and PFMOBA) were poorly adsorbed by PAC (Figure 3), it is
189 expected that PFMOAA adsorption is negligible at the tested conditions.

190 To compare the affinity of different PFASs for PAC, the PFAS removal percentages in solution
191 were plotted as a function of PFAS chain length (the sum of carbon (including branched), ether
192 oxygen, and sulfur atoms) (Figure 3(b)). The adsorbability of both legacy and emerging PFASs
193 increased with increasing chain length. PFSA were more readily removed than PFCAs of
194 matching chain length, which agrees with previous studies.^{23, 24, 28} PFECAs exhibited lower
195 adsorbabilities than PFCAs of the same chain length (e.g. PFMOBA < PFHxA), suggesting that
196 the replacement of a CF₂ group with an ether oxygen atom decreases the affinity of PFASs for
197 PAC. However, the replacement of additional CF₂ groups with ether groups resulted in small or
198 negligible affinity changes among the studied PFECAs (e.g., PFMOBA ~ PFO₂HxA).
199 Alternatively, if only the number of perfluorinated carbons were considered as a basis of
200 comparing adsorbability, the interpretation would be different. In that case, with the same
201 number of perfluorinated carbons, PFCAs have a higher affinity for PAC than mono-ether
202 PFECAs (e.g., PFPeA > PFMOBA), but a lower affinity than multi-ether PFECAs (e.g.,
203 PFPeA < PFO₃OA).

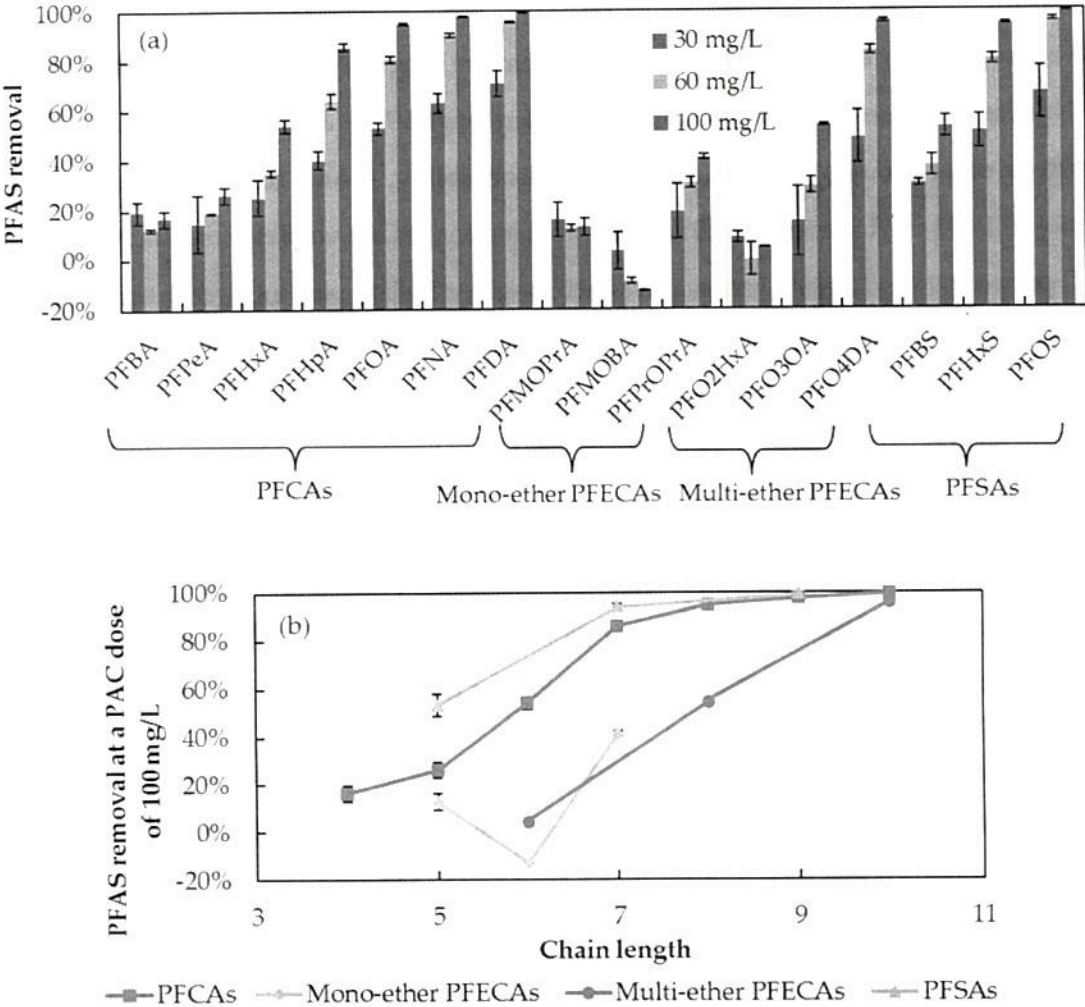


Figure 3. PFAS adsorption on PAC (a) at carbon doses of 30, 60 and 100 mg/L and (b) as a function of PFAS chain length. PAC contact time in CFR water was 1 hour. Legacy PFASs were spiked at ~1000 ng/L and the emerging PFASs were at ambient concentrations. Figures show average PFAS removal percentages, and error bars show one standard deviation of replicate experiments.

In either framework, it is clear that the presence of ether groups in PFECAs changes their propensity to leave the aqueous phase and adsorb on PAC. It can thus be inferred that the incorporation of ether groups changes physiochemical properties, such as the octanol-water

partition coefficient and aqueous solubility of PFECAs relative to PFCAs. Consequently, it is reasonable to expect that fate and transport of PFECAs in natural and engineered systems will differ from that of legacy PFCAs. For example, while PFPrOPrA ("GenX") may be less bioaccumulative than PFOA, which it is replacing, the adsorption data here suggest PFPrOPrA is less hydrophobic than PFOA. Thus, when released to the environment, PFPrOPrA has a higher tendency to remain in the aqueous phase and is more difficult to remove from drinking water sources by adsorptive means.

To the knowledge of the authors, this is the first paper reporting the behavior of recently identified PFECAs in water treatment processes. We further show that legacy PFASs continue to be a concern in the upper reaches of the CFR basin, and that PFECAs are an important class of fluorinated alternatives that dominated the PFAS signature downstream of a fluorochemical manufacturer. The relatively low concentrations of legacy PFASs in the finished drinking water of community C are consistent with data reported from this DWTP in the third unregulated contaminant monitoring rule (UCMR3) conducted by USEPA³¹. However, the detection of potentially high levels of PFECAs, and the difficulty to effectively remove not only legacy PFASs but also PFECAs with many water treatment processes, suggest the need for broader discharge control and contaminant monitoring.

Acknowledgement

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Legacy and emerging perfluoroalkyl substances are important drinking water contaminants in the Cape Fear River Watershed of North Carolina

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Supporting information includes analytical method description, 6 tables, and 5 figures.

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Analytical standards: PFASs studied in this research are listed in Table S1. For legacy PFASs, native and isotopically labeled standards were purchased from Wellington Laboratories (Guelph, Ontario, Canada). Native PFPrOPrA was purchased from Thermo Fisher Scientific (Waltham, MA). No analytical standards were available for other PFECAs.

PFAS quantification: PFAS concentrations in samples from DWTPs and adsorption tests were determined by liquid chromatography tandem mass spectrometry (LC-MS/MS) using a large-volume (0.9 mL) direct injection method. An Agilent 1100 Series LC pump and PE Sciex API 3000 LC-MS/MS system equipped with a 4.6 mm x 50 mm HPLC column (Kinetex C18 5 μ m 100Å, Phenomenex Inc.) was used for PFAS analysis. The eluent gradient is shown in Table S4 in SI. All samples, calibration standards, and quality control samples were spiked with isotopically labeled internal standards, filtered through 0.45- μ m glass microfiber syringe filters, and analyzed in duplicate. The MS transitions for PFAS analytes and internal standards are shown in Table S5 in SI. The quantitation limit (QL) was 25 ng/L for PFOS and perfluorodecanoic acid, and 10 ng/L for other legacy PFASs and PFPrOPrA. For PFECAs without analytical standards, chromatographic peak areas are reported.

PFAS concentrations along the treatment train of DWTP C were analyzed using a Waters Acquity ultra performance liquid chromatograph interfaced with a Waters Quattro Premier XE triple quadrupole mass spectrometer (Waters, Milford, MA, USA) after solid phase extraction. Method details are described elsewhere.¹ The QL for all PFASs with analytical standards was 0.2 ng/L, and peak areas were recorded for PFECAs without standards.

Table S1. Perfluoroalkyl substances (PFASs) detected in the Cape Fear River (CFR) watershed

Compound	Molecular weight	Formula	CAS #	# of perfluorinated carbons	Chain length (including all C, O and S)
Perfluorocarboxylic acids (PFCAs)					
Perfluorobutanoic acid (PFBA)	214.0	C ₄ HF ₇ O ₂	375-22-4	3	4
Perfluoropentanoic acid (PFPeA)	264.0	C ₅ HF ₉ O ₂	2706-90-3	4	5
Perfluorohexanoic acid (PFHxA)	314.1	C ₆ HF ₁₁ O ₂	307-24-4	5	6
Perfluoroheptanoic acid (PFHpA)	364.1	C ₇ HF ₁₃ O ₂	375-85-9	6	7
Perfluorooctanoic acid (PFOA)	414.1	C ₈ HF ₁₅ O ₂	335-67-1	7	8
Perfluorononanoic acid (PFNA)	464.1	C ₉ HF ₁₇ O ₂	375-95-1	8	9
Perfluorodecanoic acid (PFDA)	514.1	C ₁₀ HF ₁₉ O ₂	335-76-2	9	10
Perfluorosulfonic acids (PFSAs)					
Perfluorobutane sulfonic acid (PFBS)	300.1	C ₄ HF ₉ SO ₃	29420-49-3	4	5
Perfluorohexane sulfonic acid (PFHxS)	438.2	C ₆ HF ₁₃ SO ₃	355-46-4	6	7
Perfluorooctane sulfonic acid (PFOS)	500.1	C ₈ HF ₁₇ SO ₃	111873-33-7	8	9
Perfluoroalkyl ether carboxylic acids with one ether group (mono-ether PFECAs)					
Perfluoro-2-methoxyacetic acid (PFMOAA)	180.0	C ₃ HF ₅ O ₃	674-13-5	2	4
Perfluoro-3-methoxypropanoic acid (PFMOPrA)	230.0	C ₄ HF ₇ O ₃	377-73-1	3	5
Perfluoro-4-methoxybutanoic acid (PFMOBA)	280.0	C ₅ HF ₉ O ₃	863090-89-5	4	6
Perfluoro-2-propoxypropanoic acid (PFPrOPrA)	330.1	C ₆ HF ₁₁ O ₃	13252-13-6	5	7
Perfluoroalkyl ether carboxylic acids with multiple ether group (multi-ether PFECAs)					
Perfluoro(3,5-dioxahexanoic) acid (PFO2HxA)	246.0	C ₄ HF ₇ O ₄	39492-88-1	3	6
Perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA)	312.0	C ₅ HF ₉ O ₅	39492-89-2	4	8
Perfluoro(3,5,7,9-tetraoxadecanoic) acid (PFO4DA)	378.1	C ₆ HF ₁₁ O ₆	39492-90-5	5	10

Table S2. Operational conditions of DWTP C on sampling day (August 18, 2014)

Parameter	Value
Raw water ozone dose	3.1 mg/L
Raw water total organic carbon concentration	6.0 mg/L
Aluminum sulfate coagulant dose	43 mg/L
Coagulation pH	5.70
Settled water ozone dose	1.3 mg/L
Settled water total organic carbon concentration	1.90 mg/L
Empty bed contact time in biological activated carbon filters	9.4 minutes for granular activated carbon layer 2.3 minutes for sand layer
Medium pressure UV dose	25 mJ/cm ²
Free chlorine dose	1.26 mg/L as Cl ₂
Free chlorine contact time	17.2 hours

Table S3. Water quality characteristics of surface water used in adsorption tests

Non-purgeable organic carbon (mg/L)	Ultraviolet absorbance at a wavelength of 254 nm	pH	Alkalinity (mg/L as CaCO ₃)	Conductivity (μS/cm)
9.036	0.399	7.53	19	133.5

Table S4. LC gradient method for PFAS analysis

Time (min)	Mobile Phase A% (v/v)	Mobile Phase B%	Flow Rate (mL/min)
0 – 2	95	5	0.9
2 – 5	95	5	0.9
5 – 10	95 → 10	5 → 90	0.9
10 – 10.1	10	90	0.9
10.1 – 14	10 → 95	90 → 5	0.9

Mobile phase A: 2 mM ammonium acetate in ultrapure water with 5% methanol

Mobile phase B: 2 mM ammonium acetate in acetonitrile with 5% ultrapure water

Table S5. MS transitions for PFAS Analysis

	Compound	MS/MS Transition	Internal standard
Legacy PFASs	PFBA	212.8 → 168.8	13C4-PFBA
	PFPeA	262.9 → 218.8	13C2- PFHxA
	PFHxA	313.6 → 268.8	13C2- PFHxA
	PFHpA	362.9 → 318.8	13C4- PFOA
	PFOA	413.0 → 368.8	13C4- PFOA
	PFNA	463.0 → 418.8	13C4- PFOA
	PFDA	513.1 → 68.8	13C2-PFDA
	PFBS	299.1 → 98.8	18O2-PFHxS
	PFHxS	399.1 → 98.8	18O2-PFHxS
	PFOS	498.9 → 98.8	13C4-PFOS
PFECAs	PFMOAA	180.0 → 85.0	N/A
	PFMOPrA	229.1 → 184.9	N/A
	PFMOBA	279.0 → 234.8	N/A
	PFPrOPrA	329.0 → 284.7	13C2- PFHxA
	PFO2HxA	245.1 → 85.0	N/A
	PFO3OA	311. → 84.9	N/A
	PFO4DA	377.1 → 85.0	N/A
Internal standards	Perfluoro-n-[1,2,3,4- ¹³ C ₄]butanoic acid (13C4-PFBA)	217.0 → 172	Not applicable
	Perfluoro-n-[1,2- ¹³ C ₂]hexanoic acid (13C2-PFHxA)	315.1 → 269.8	
	Perfluoro-n-[1,2,3,4- ¹³ C ₂]octanoic acid (13C4-PFOA)	417.0 → 372.0	
	Perfluoro-n-[1,2- ¹³ C ₂]decanoic acid (13C2-PFDA)	515.1 → 469.8	
	Sodium perfluoro-1-hexane[¹⁸ O ₂]sulfonate (18O2-PFHxS)	403.1 → 83.8	
	Sodium perfluoro-1-[1,2,3,4- ¹³ C ₄]octane sulfonate (13C4-PFOS)	502.9 → 79.9	

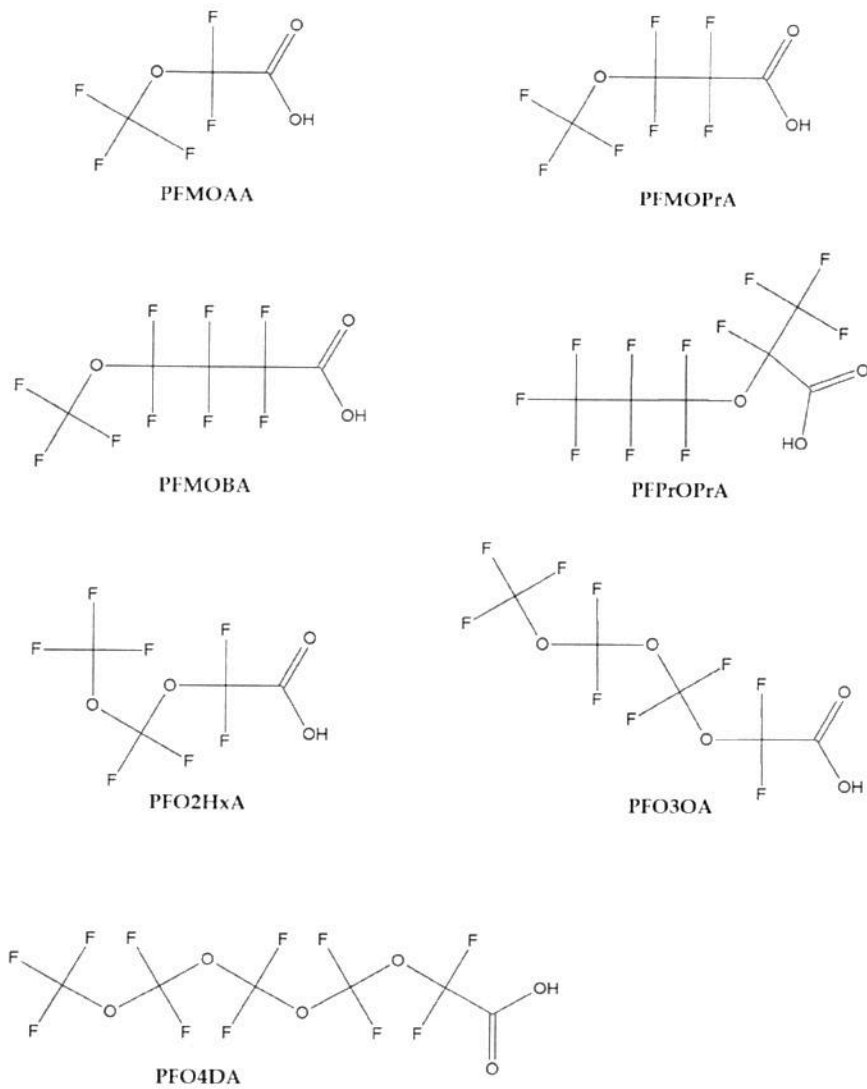
Table S6. Maximum, minimum, mean and median concentrations (ng/L) of PFASs in CFR watershed surface water as drinking water sources. *

	Community A				Community B				Community C			
	max	min	median	mean	max	min	median	mean	max	min	median	mean
PFBA	99	<10	26	33	38	<10	12	12	104	<10	12	22
PFPeA	191	14	44	62	38	<10	19	19	116	<10	30	36
PFHxA	318	<10	48	78	42	<10	<10	11	24	<10	<10	<10
PFHpA	324	<10	39	67	85	<10	<10	11	24	<10	<10	<10
PFOA	137	<10	34	46	32	<10	<10	<10	17	<10	<10	<10
PFNA	38	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
PFDA	35	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25
PFBS	80	<10	<10	<10	11	<10	<10	<10	<10	<10	<10	<10
PFHxS	193	<10	10	14	14	<10	<10	<10	14	<10	<10	<10
PFOS	346	<25	29	44	43	<25	<25	<25	40	<25	<25	<25
PFPPrOPrA	<10	<10	<10	<10	10	<10	<10	<10	4560	55	304	631
PFOA+PFOS	447	0	64	90	59	0	0	9	55	<10	<10	<10
Σ PFASs**	1502	18	212	355	189	0	47	62	4696	55	345	710

* Concentrations < quantification limits were considered as zero to calculate means and Σ PFASs.

** Other PFECAs were present in water samples from community C but could not be quantified and were therefore not included in Σ PFASs

Figure S1. Molecular structures of PEFCAs in this study



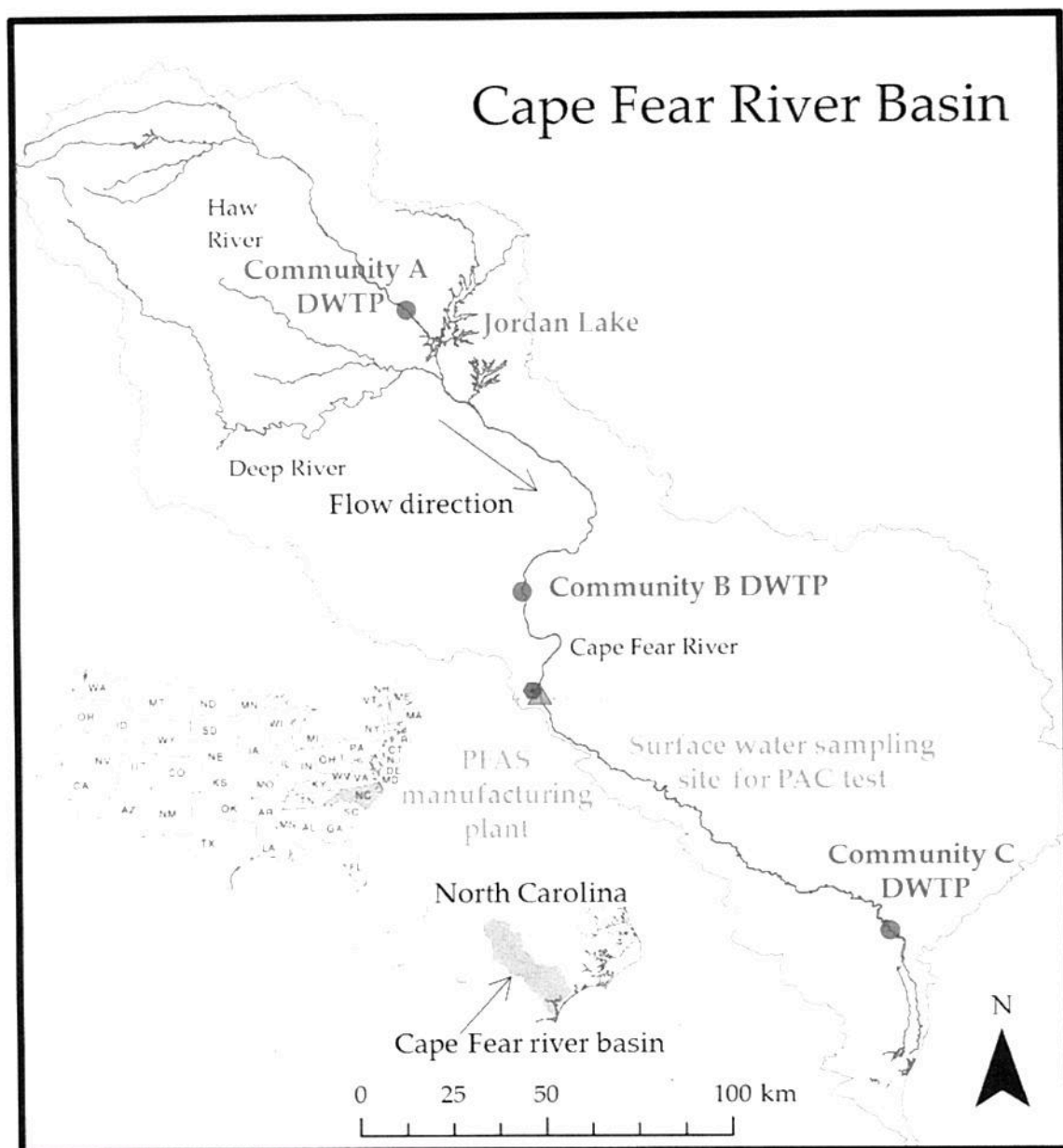
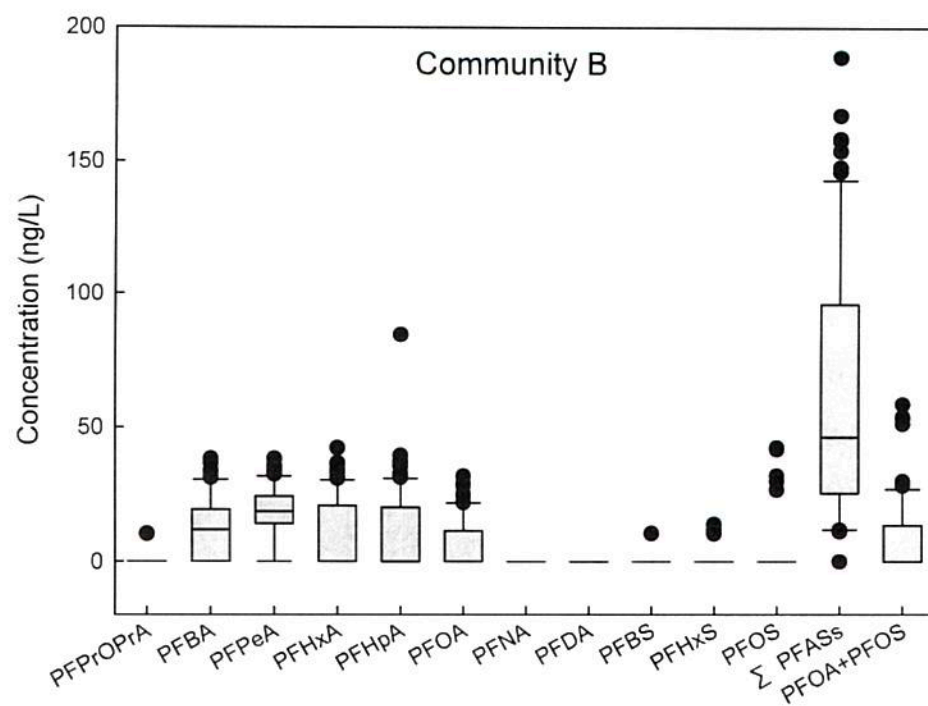
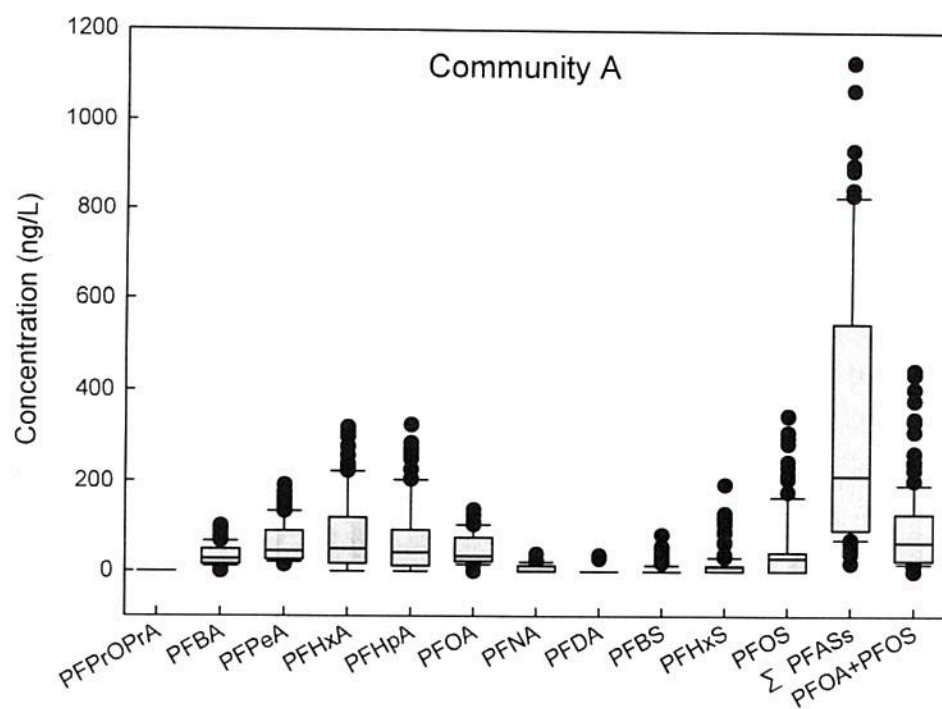


Figure S2. Sampling sites in the Cape Fear River watershed, North Carolina



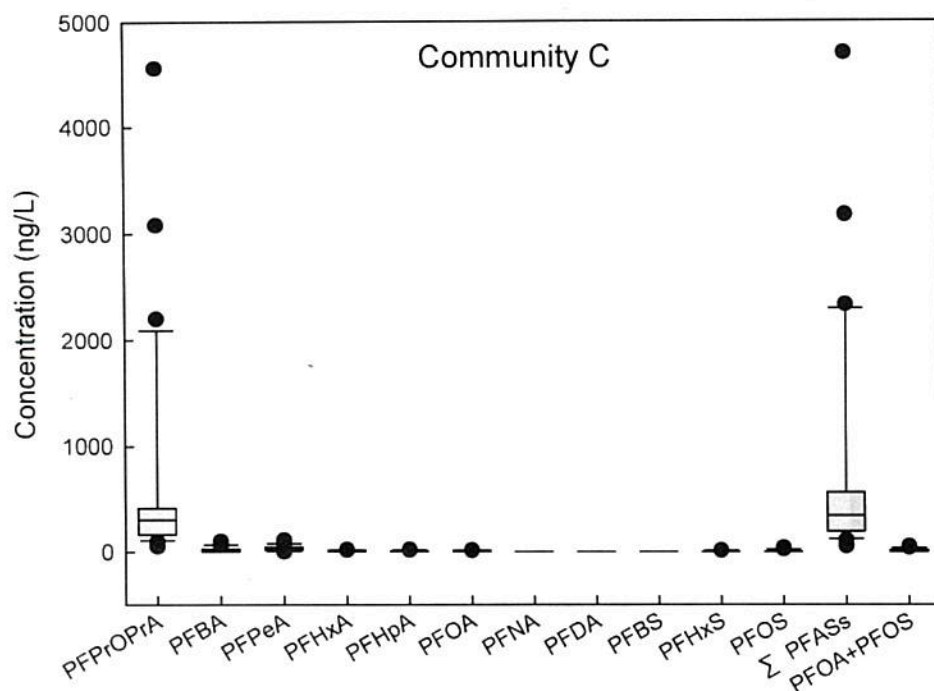


Figure S3. PFAS concentration distributions in the CFR watershed at three drinking water intakes. Concentrations < quantification limits were considered as zero. The upper and lower edges of a box represent the 75th and 25th percentile, respectively; the middle line represents the median; the upper and lower bars represent the 90th and 10th percentile, respectively; the dots represent outliers (>90th or <10th percentile).

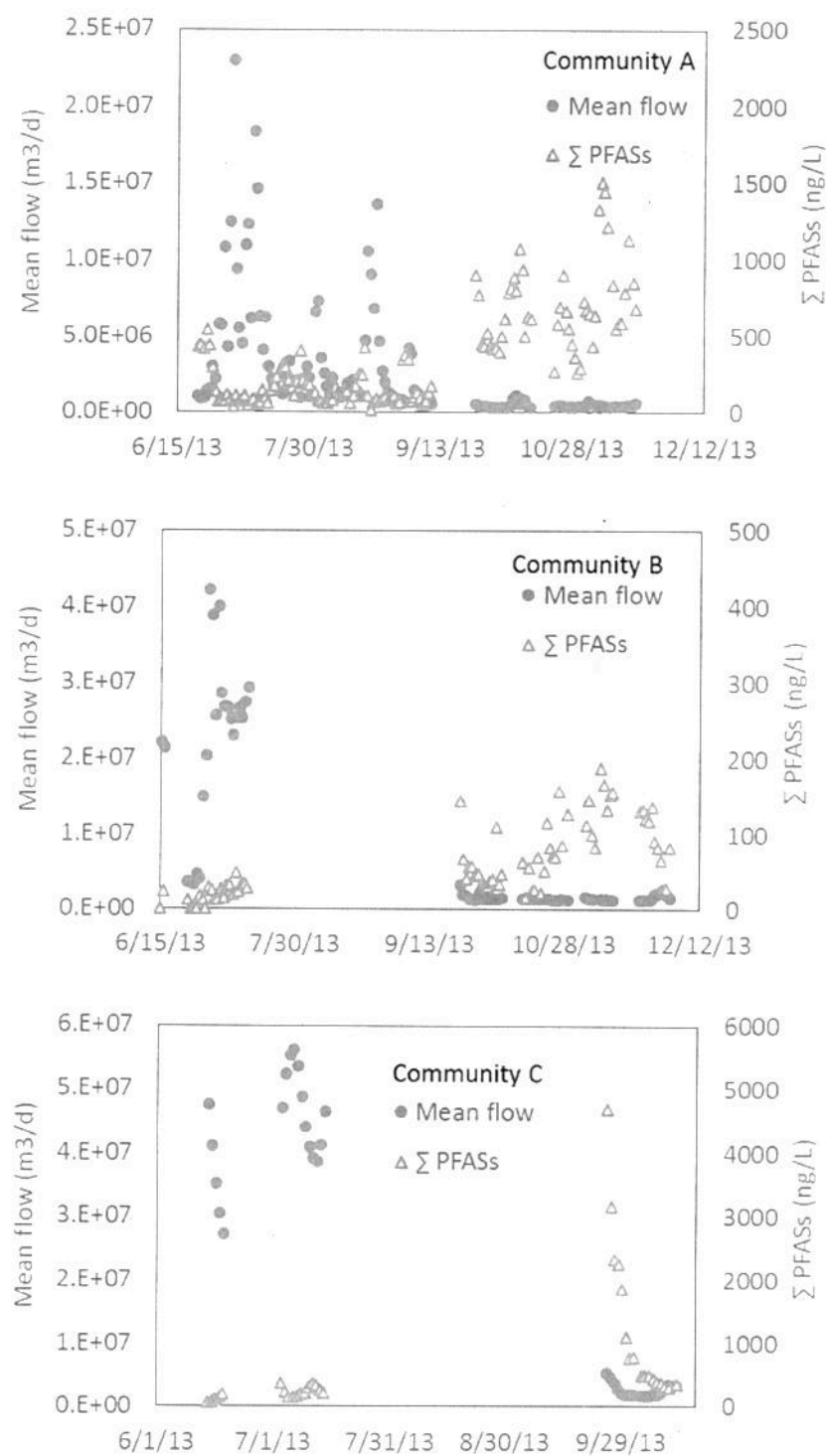


Figure S4. Total PFAS concentrations in the source water and stream flow at the three studied DWTPs. Stream flow data were acquired from US Geological Survey stream gage records

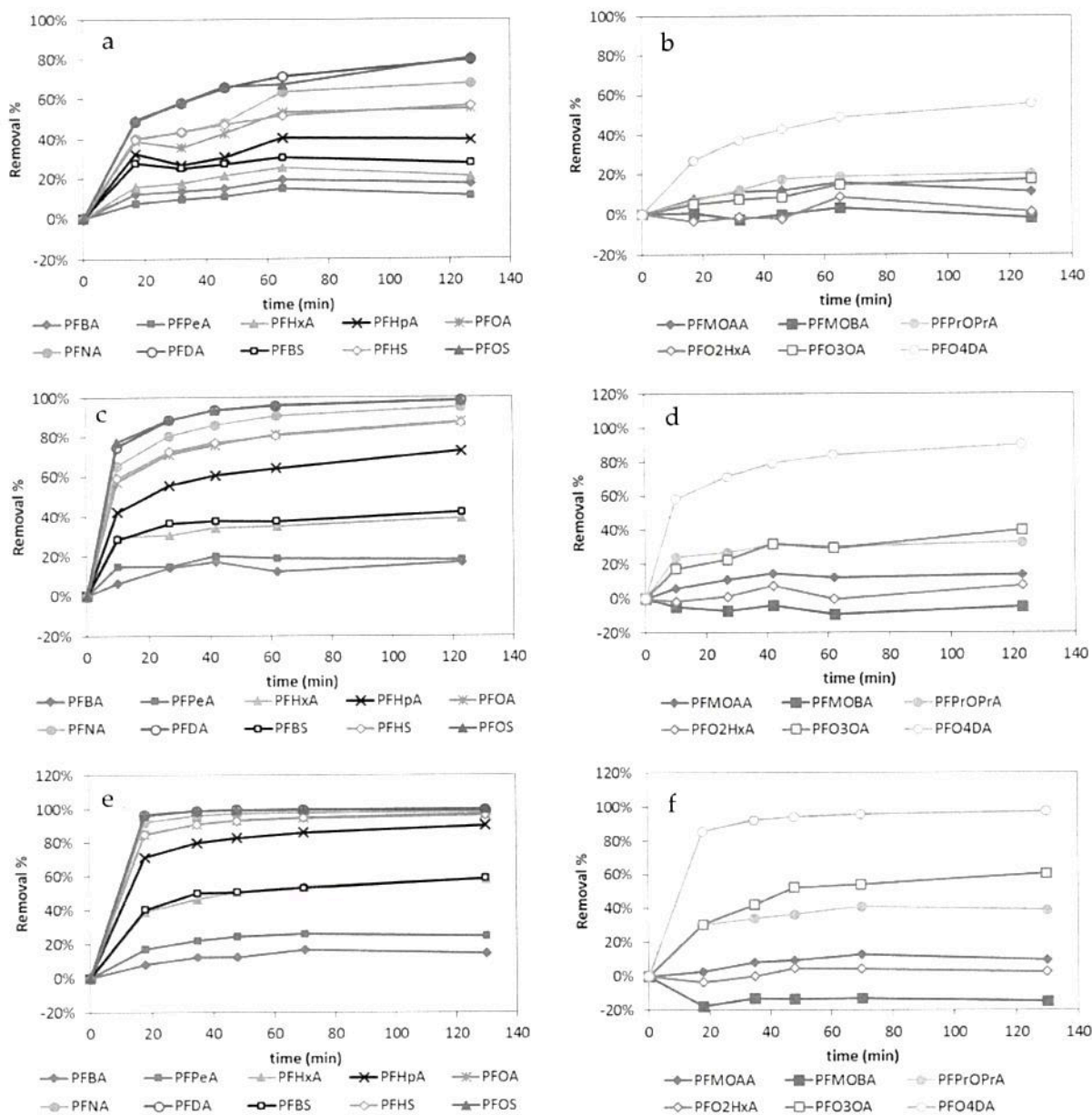


Figure S5. PFAS adsorption on PAC at carbon doses of (a, b) 30 mg/L, (c, d) 60 mg/L and (e, f) 100 mg/L. Figures show average PFAS removal percentages of duplicate tests.

Reference

1. Nakayama, S.; Strynar, M. J.; Helfant, L.; Egeghy, P.; Ye, X.; Lindstrom, A. B., Perfluorinated compounds in the Cape Fear drainage basin in North Carolina. *Environmental Science & Technology* **2007**, *41*, (15), 5271-5276.

[illegible]

NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	12/5/2013	2013112060141AM	HCIC-22	0.08	EPA 524 <	SE1	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	3/11/2014	201401120485AM	HCIC-22	0.08	EPA 524 <	SE2	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	6/9/2014	201406100211AM	HCIC-22	0.08	EPA 524 <	SE3	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	9/8/2014	201409090436AM	HCIC-22	0.08	EPA 524 <	SE4	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	12/5/2013	2013112060141AM	molysbdenum	1	EPA 200.8 <	SE1	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	3/11/2014	201401120485AM	molysbdenum	1	EPA 200.8 <	SE2	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	6/9/2014	201406100211AM	molysbdenum	1	EPA 200.8 <	SE3	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	9/8/2014	201409090436AM	molysbdenum	1	EPA 200.8 <	SE4	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	12/5/2013	2013112060141AM	PFBS	0.09	EPA 537 <	SE1	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	3/11/2014	201401120485AM	PFBS	0.09	EPA 537 <	SE2	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	6/9/2014	201406100211AM	PFBS	0.09	EPA 537 <	SE3	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	9/8/2014	201409090436AM	PFBS	0.09	EPA 537 <	SE4	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	12/5/2013	2013112060141AM	PFHqA	0.01	EPA 537 <	SE1	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	3/11/2014	201401120485AM	PFHqA	0.01	EPA 537 <	SE2	AM	4	NC
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NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	12/5/2013	2013112060141AM	PFHqS	0.03	EPA 537 <	SE1	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	3/11/2014	201401120485AM	PFHqS	0.03	EPA 537 <	SE2	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	6/9/2014	201406100211AM	PFHqS	0.03	EPA 537 <	SE3	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	9/8/2014	201409090436AM	PFHqS	0.03	EPA 537 <	SE4	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	12/5/2013	2013112060141AM	PFNA	0.02	EPA 537 <	SE1	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	3/11/2014	201401120485AM	PFNA	0.02	EPA 537 <	SE2	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	6/9/2014	201406100211AM	PFNA	0.02	EPA 537 <	SE3	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	9/8/2014	201409090436AM	PFNA	0.02	EPA 537 <	SE4	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	12/5/2013	2013112060141AM	PFQ	0.02	EPA 537 <	SE1	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	3/11/2014	201401120485AM	PFQ	0.02	EPA 537 <	SE2	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	6/9/2014	201406100211AM	PFQ	0.02	EPA 537 <	SE3	AM	4	NC
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NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	12/5/2013	2013112060141AM	PFOS	0.04	EPA 537 <	SE1	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	3/11/2014	201401120485AM	PFOS	0.04	EPA 537 <	SE2	AM	4	NC
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NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	3/11/2014	201401120485AM	PFNA	0.3	EPA 200.8 <	SE2	AM	4	NC
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NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	12/5/2013	2013112060141AM	PFNA	0.3	EPA 200.8 <	SE1	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	3/11/2014	201401120485AM	PFNA	0.3	EPA 200.8 <	SE2	AM	4	NC
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NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	6/9/2014	201406100211AM	PFNA	0.3	EPA 200.8 <	SE3	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	9/8/2014	201409090436AM	PFNA	0.3	EPA 200.8 <	SE4	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	12/5/2013	2013112060141AM	PFNA	0.3	EPA 200.8 <	SE1	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	3/11/2014	201401120485AM	PFNA	0.3	EPA 200.8 <	SE2	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	6/9/2014	201406100211AM	PFNA	0.3	EPA 200.8 <	SE3	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	9/8/2014	201409090436AM	PFNA	0.3	EPA 200.8 <	SE4	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	12/5/2013	2013112060141AM	PFNA	0.3	EPA 200.8 <	SE1	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	3/11/2014	201401120485AM	PFNA	0.3	EPA 200.8 <	SE2	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	6/9/2014	201406100211AM	PFNA	0.3	EPA 200.8 <	SE3	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	9/8/2014	201409090436AM	PFNA	0.3	EPA 200.8 <	SE4	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP	SW	7	EPDTS from Swamy WTP	EP	60424 U99001	12/5/2013	2013112060141AM	PFNA	0.3	EPA 200.8 <	SE1	AM	4	NC
NC0465010	CFJUA - Wilmington	L	S	Swamy WTP														

